PATENT SPECIFICATION (11) 1 292 025

1 292 025

NO DRAWINGS

(21) Application No. 49552/68 (22) Filed 18 Oct. 1968

(23) Complete Specification filed 20 Oct. 1969

(45) Complete Specification published 11 Oct. 1972

(51) International Classification B01D 53/22//C22C 5/00

(52) Index at acceptance

B1L 7C

C7A B230 B23Y B279 B289 B309 B319 B339 B349 B369 B389 B399 B419 B439 B459 B489 B519 B539 B549 B559 B610 B613 B616 B619 B621 B624 B627 B62X B635 B63X B63Y B661 B663 B665 B667 B669 B66X B670

C7B 1B 1H

(72) Inventor ALAN SYDNEY DARLING

(54) IMPROVEMENTS IN OR RELATING TO THE SEPARATION OF HYDROGEN FROM GASEOUS MIXTURES CONTAINING HYDROGEN

(71) We, JOHNSON, MATTHEY & COMPANY LIMITED, a British Company, of 78, Hatton Garden, London, E.C.1, do hereby declare the invention for which we pray that a Patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the separation of hydrogen from a gaseous mixture containing hydrogen by diffusion through a hydrogen permeable membrane.

A well-known method of separating hydrogen from a gaseous mixture containing hydrogen or of purifying impure hydrogen gas is to bring the gaseous mixture or the impure hydrogen into contact with one surface of a heated palladium diffusion membrane or diffusion tube, which acts as a filter, allowing pure hydrogen to diffuse through the membrane or tube whilst preventing the passage of other constituents of the gas or gaseous mixture, the pure hydrogen being collected as required.

The permeability of hydrogen through a diffusion membrane or diffusion tube depends, as is known, on the temperature at which it is operated and also on the pressure differential maintained between the high pressure side and the low pressure side of the membrane or tube, that is to say, the side at which the impure gas contacts the membrane or tube and the side at which the pure hydrogen issues. The higher is this pressure differential, the greater is the permeability of the membrane or tube.

Permeability or diffusion rate also depends on the material from which the membrane or tube is made and it has been suggested to use pure palladium, palladium/silver alloys and palladium/boron alloys for this purpose.

According to one feature of this invention the diffusion membrane or tube comprises an imperforate substrate of nickel, iron, vanadium, tantalum or niobium or an alloy containing any one or more of these metals the substrate being coated on both faces thereof with a film of palladium or a palladium alloy which is discontinuous or porous or both discontinuous and porous.

Where the coating of palladium is discontinuous, at least 25% and preferably 75% to 80% of the substrate of the said metal or alloy is coated with the palladium. Preferably the palladium is 99% pure but, if desired palladium alloys, for example palladium/silver alloys containing between 10 and 40% silver may be used.

The coating of palladium may be applied by, for example, printing techniques, electro deposition or metal spraying.

Examples of membranes and diffusion tubes are as follows:

1) Palladium/nickel/palladium
2) Palladium/iron/palladium
3) Palladium/vanadium/palladium
4) Palladium/tantalum/palladium
5) Palladium/niobium/palladium

In one example the palladium coating was bonded to both sides of the said metal or alloy by metal spraying and subsequent heat treatment. The palladium coating was originally 0.025 inch thick and the substrate metal was 0.500" prior to rolling both to a combined foil thickness within the range 0.0005 inch to 0.0016 inch.

Our experiments indicated that hydrogen diffusion rates for the iron and nickel foils were somewhat lower than for palladium alone but the vanadium and tantalum foils produced diffusion rates higher than for palladium alone.

Using a gas having a composition of 99.7% H_2 and with 0.3% total impurities at a temperature of 500°C, the diffusion rates obtained with a tantalum or niobium membrane covered over approximately 80%

of the area of both surfaces with palladium, were 10-40% higher than would have been obtained over the pressure ranges investigated with pure palladium membranes of comparable thickness.

The composite foils, for use as diffusion membranes or tubes in accordance with this invention, are more economical to manufacture than the foils used hitherto owing to the fact that considerably less palladium or palladium alloy is used since the palladium or palladium alloy coating may be as little as 0.0005 inch thick. Furthermore, membranes of tantalum, vanadium and niobium are considerably stronger at high temperatures than palladium or silver palladium alloy membranes. This practical consideration is a valuable advantage and leads to simplification of fuel cell design.

The invention also includes a method of separating hydrogen from gaseous mixtures containing hydrogen or purifying hydrogen gas wherein the gaseous mixture or the impure hydrogen is brought into contact with one surface of a diffusion membrane or tube which comprises a substrate of nickel, iron, vanadium, tantalum or niobium metal or an alloy containing one or more of these metals coated on at least one face thereof with a film of palladium or of a palladium alloy which is discontinuous or porous or both discontinuous and porous.

A membrane or tube made in accordance with this invention may be used to replace the palladium/silver alloy diffusion element in the preparation of heavy water as described in our earlier Patent No. 973820.

WHAT WE CLAIM IS:

1. A membrane or tube permeable by hydrogen by diffusion which comprises an imperforate substrate-membrane or -tube of nickel, iron, vanadium, tantalum or niobium metal or an alloy containing one or more of these metals the substrate being coated on both faces thereof with a film of palladium or of a palladium alloy, which is discontinuous or porous or both discontinuous and porous.

2. A diffusion membrane or tube coated with a discontinuous film according to claim 1 wherein 25 to 80% of the area of the substrate is covered with palladium metal or palladium alloy.

3. A diffusion membrane or tube according to claim 1 or 2 wherein the palladium is 99% pure.

4. A diffusion membrane or tube according to claim 1 or 2 wherein the palladium alloy contains from 60% to 90% by weight of palladium.

5. A diffusion membrane or tube according to any one of the preceding claims wherein the palladium alloy contains 10 to 40% by weight of silver.

6. A diffusion membrane or tube according to any one of the preceding claims having a thickness within the range 0.0005 to 0.0016 inch.

7. A method of making a hydrogen diffusion membrane or diffusion tube as claimed in any one of the preceding claims wherein the palladium or palladium alloy is applied by printing techniques, electrodeposition or metal spraying in the form of a film which is discontinuous or porous or both to the imperforate metal or alloy substrate.

8. A method according to claim 7 wherein the said film is applied in a thickness up to 0.025 inch to the metal or alloy substrate having a thickness of 0.500 inch and thereafter the film and the substrate together are rolled down to a combined thickness within the range 0.0005 inch to 0.0016 inch.

9. A method of separating hydrogen from a gaseous mixture containing hydrogen or of purifying hydrogen gas wherein the gaseous mixture or the impure hydrogen is brought into contact with a diffusion membrane or tube as claimed in any one of claims 1 to 6.

10. A hydrogen diffusion membrane or diffusion tube as claimed in claim 1 substantially as hereinbefore described.

11. A method of making a hydrogen diffusion membrane or tube substantially as hereinbefore described.

12. A method of separating hydrogen from a gaseous mixture containing hydrogen or of purifying hydrogen as claimed in claim 9 substantially as hereinbefore described.

13. A method of separating hydrogen isotopes in the preparation of heavy water by the electrolysis of a suitable electrolyte or by electrolytic migration in which there is used a hydrogen diffusion membrane or tube as claimed in any one of claims 1 to 6.

14. Heavy water when produced by the method claimed in claim 13.

WITHERS & SPOONER,
Chartered Patent Agents,
148-150 Holborn,
London, E.C.1
Agents for the Applicants.

Printed for Her Majesty's Stationery Office by The Tweeddale Press Ltd., Berwick-upon-Tweed, 1972. Published at the Patent Office, 25 Southampton Buildings, London WC2A 1AY from which copies may be obtained.